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LETTER

Evidence of 1991–2013 decrease of biogenic secondary organic aerosol in response to SO_2 emission controls

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Abstract

Air quality policy to decrease fine particulate matter mass concentrations ($PM_{2.5}$) in the US has mainly targeted sulfate aerosol through controls on sulfur dioxide (SO_2) emissions. Organic aerosol (OA) instead of sulfate is now the dominant component of total $PM_{2.5}$. Long-term surface observations (1991–2013) in the Southeast US in summer show parallel decreases in sulfate (2.8%–4.0% a^{-1}) and OA (1.6%–1.9% a^{-1}). Decline of anthropogenic OA emissions is uncertain but is unlikely to fully explain this trend because most OA in the Southeast US in summer is biogenic. We conducted a 1991–2013 simulation with the GEOS-Chem chemical transport model including inventory decreases in anthropogenic SO_2, NO_x, and volatile organic compounds (VOCs) emissions, constant anthropogenic primary OA emissions, and a new mechanism of aqueous-phase SOA formation from isoprene. This simulation reproduces the observed long-term decreases of sulfate and OA, and attributes the OA decrease to decline in the OA yield from biogenic isoprene as sulfate decreases (driving lower aqueous aerosol volume and acidity). Interannual OA variability in the model (mainly driven by isoprene) is also well correlated with observations. This result provides support for a large air quality co-benefit of SO_2 emission controls in decreasing biogenic OA as well as sulfate.

1. Introduction

Air quality policy in the US to decrease mass concentrations of fine particulate matter ($PM_{2.5}$, mass concentration of particles less than 2.5 μm diameter) has focused primarily on sulfur dioxide (SO_2) emission controls. Anthropogenic SO_2 emissions decreased by 3.3% a^{-1} over the 1991–2013 period according to the US Environmental Protection Agency (EPA 2015). This has successfully decreased the sulfate component of $PM_{2.5}$ by 2.7% a^{-1} nationwide over 1992–2010 (Hand *et al* 2012). Organic aerosol (OA) is now the dominant component of $PM_{2.5}$ in the eastern US in summer and particularly in the south (Attwood *et al* 2014, Kim *et al* 2015), but there is no clear emission control strategy to target that component. OA has a primary combustion source (POA) but appears to be predominantly secondary (SOA) in summer, formed when oxidation products of mostly biogenic volatile organic compounds (VOCs) condense to pre-existing aerosol (Weber *et al* 2007, Kleindienst *et al* 2010, Blanchard *et al* 2016). Recent field studies and models for the Southeast US in summer have pointed to isoprene, the dominant biogenic VOC emitted by vegetation, as a major contributor to OA (Kim *et al* 2015, Xu *et al* 2015).

Long-term observations of speciated $PM_{2.5}$ at Southeast US sites show a decrease in summertime OA of 0.9% a^{-1} over 1992–2013 and 1.5% a^{-1} over 1998–2013 (Attwood *et al* 2014). The contribution to this decrease in anthropogenic OA sources is unclear but unlikely to fully explain the observed OA trend. Source apportionment studies and carbon isotope measurements indicate that anthropogenic sources

account for only 5%–10% of OA concentrations in the Southeast US in summer in Atlanta, Georgia (Zheng *et al* 2007) and at a regionally representative rural site (Blanchard *et al* 2008). A regional model analysis finds that anthropogenic sources contribute 28% of OA in the Southeast US in summer (Kim *et al* 2015). Anthropogenic VOC emissions decreased by 1.6% a^{-1} over the 1991–2013 period (EPA 2015) but the link to SOA is uncertain (Attwood *et al* 2014). The EPA reports trends in annual primary $PM_{2.5}$ emissions but not the POA component (Blanchard *et al* 2013, EPA 2015). Blanchard *et al* (2016) estimate large decreases in annual mean combustion-derived OA (3.2%–4.2% a^{-1}) at urban sites in the Southeast US and attribute most of this trend to decline in vehicle emissions. On the other hand, in the rural Southeast US principal component analysis and multiple linear regression applied to long-term (1999–2013) observations show no significant trend in the anthropogenic OA component (Hidy *et al* 2014, Blanchard *et al* 2016).

Observations of OA in the Southeast US indicate a ~30% contribution from isoprene epoxydiols (IEPOX SOA) that correlates strongly with sulfate (Budisulistiorini *et al* 2015, Hu *et al* 2015, Xu *et al* 2015, Marais *et al* 2016). This correlation appears to reflect acid-catalyzed aqueous-phase IEPOX SOA formation (Marais *et al* 2016). Biogenic SOA produced from glyoxal by aqueous-phase aerosol pathways (Ervens and Volkamer 2010, McNeill *et al* 2012) would also depend on the availability of sulfate as a source of aerosol water (Nguyen *et al* 2015). One might therefore expect a decrease in biogenic SOA as SO_2 emissions decrease, and this has been suggested as a major co-benefit of SO_2 emission controls (Surratt *et al* 2010, Carlton and Turpin 2013, Pye *et al* 2013, Xu *et al* 2015, Marais *et al* 2016, Xu *et al* 2016).

Anthropogenic emissions of reactive nitrogen oxides ($NO_x \equiv NO + NO_2$) have also decreased over the past decade to improve ozone air quality. Nitrate is a negligibly small component of $PM_{2.5}$ in the Southeast in summer because of high temperatures (Kim *et al* 2015). A potentially larger effect is that the SOA yield from VOC oxidation depends on whether this oxidation proceeds by high-NO_x or low-NO_x pathways (Pye *et al* 2010).

Here we conduct a 1991–2013 simulation of aerosol chemistry with the GEOS-Chem chemical transport model (CTM), including long-term trends in anthropogenic SO_2, NO_x, and VOC emissions as well as meteorological variability. We show that the observed OA trend in the Southeast US in summer can be explained at least in part by a decrease in isoprene SOA driven by decreasing SO_2 emissions. This result has major implications for air quality management as evidence of the co-benefit of SO_2 emission controls for decreasing $PM_{2.5}$.

2. Observed 1991–2013 trends in Southeast US sulfate and organic aerosol

Figure 1 shows time series of summertime average concentrations of sulfate and OA from the Southeastern Aerosol Research and Characterization (SEARCH) (1998–2013) (Edgerton *et al* 2005) and Interagency Monitoring of Protected Visual Environments (IMPROVE) (1991–2013) (Solomon *et al* 2014) networks in the Southeast US. There are also observations at Chemical Speciation Network (CSN) sites, but a shift in carbonaceous aerosol sampling and analysis protocols in 2007–2009 (Solomon *et al* 2014) obfuscates trend analysis. SEARCH sites are a mix of rural, urban, and suburban (Edgerton *et al* 2005); IMPROVE sites are mainly rural (Solomon *et al* 2014). Samples at both networks are collected every 3 days (Chow *et al* 2010). Measurements are reported as mass concentration of organic carbon (OC), and are converted here to OA using a mass conversion factor of 2.2 (OA/OC = 2.2) representative of summertime conditions in the Southeast US (Canagaratna *et al* 2015, Xu *et al* 2015). OA averages 30% lower at IMPROVE than SEARCH sites due to differences in measurement protocols (Chow *et al* 2010, Kim *et al* 2015) and greater urban influence at SEARCH sites (Blanchard *et al* 2016).

Mean decline in sulfate is 4.0% a^{-1} at SEARCH and 2.8% a^{-1} at IMPROVE sites, as compared to a national trend of 2.7% a^{-1} (Hand *et al* 2012). Mean decline in OA is 1.9% a^{-1} at SEARCH and 1.6% a^{-1} at IMPROVE sites. Figure 1 further illustrates how OA instead of sulfate is now the dominant component of total $PM_{2.5}$ in the Southeast US in summer. The relationship between the trend in summertime sulfate and OA is 0.48 μg OA per μg sulfate at SEARCH and 0.37 μg OA per μg sulfate at IMPROVE, similar to interannual relationships previously reported by Blanchard *et al* (2016).

Figure 1 focuses on summertime when biogenic OA dominates. We find that wintertime (December–February) OA shows a decreasing trend similar to summer, 2.9% a^{-1} at SEARCH and 1.6% a^{-1} at IMPROVE. Wintertime OA mostly originates from biomass burning (residential heating and prescribed burns) and vehicles. Zheng *et al* (2007) use a chemical mass balance receptor model to estimate that the vehicle contribution to OA in Atlanta is 0.39 $\mu g\ m^{-3}$ (11% of OA) in summer but 1.46 $\mu g\ m^{-3}$ (30% of OA) in winter, in part because vehicles emit more OA in winter than summer (Zheng *et al* 2002, Zheng *et al* 2007, Chen *et al* 2012). Residential heating and prescribed burns are absent in summer (Tian *et al* 2009). Apart from extreme events such as the fall 2016 fires (Samuel 2016), wildfires and agricultural fires make little contribution to OA (< 20% of total OA) in the Southeast (Park *et al* 2007, Tian *et al* 2009, Kim *et al* 2015). We do not attempt to explain the wintertime OA trend here, but the causes would have to be different than in summer and we view the

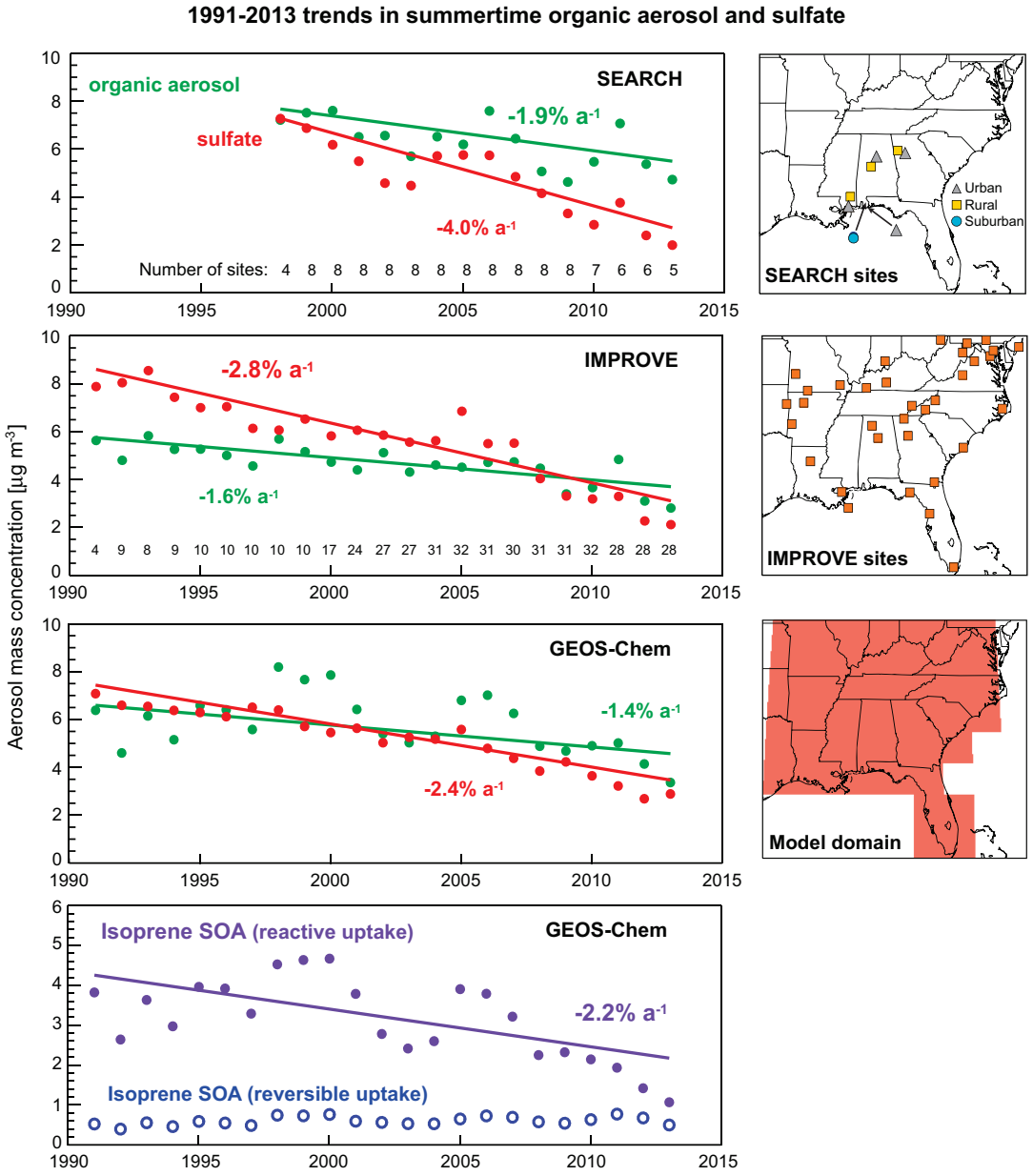

Figure 1. 1991–2013 trends of sulfate and organic aerosol (OA) mass concentrations in the Southeast US in summer (June–August). The top three panels are observed means from the SEARCH and IMPROVE networks and simulated regional means from the GEOS-Chem model. The number of sites used each year to estimate OA is given inset. Maps show monitoring sites and model domain. Trends are obtained with the Theil-Sen estimator (Theil 1950) and are significant at the 95% confidence level. The bottom panel shows the trend in isoprene secondary organic aerosol (SOA) simulated in GEOS-Chem with a scheme involving aqueous-phase reactive uptake of isoprene oxidation products (Marais *et al* 2016) and an alternate scheme involving reversible uptake of isoprene oxidation products to pre-existing OA (Pye *et al* 2010).

similarity of trends as mostly coincidental. Combining the 3.2%–4.2% a^{-1} decrease in combustion-derived OC inferred by Blanchard *et al* (2016) with a 5%–10% contribution of this source to summertime OA in the Southeast (Zheng *et al* 2007, Blanchard *et al* 2008) would imply an overall OA trend of only 0.16%–0.42% a^{-1}, much less than observed in figure 1.

3. Modeled 1991–2013 trends of Southeast US sulfate and organic aerosol

We compare the observed 1991–2013 trends of figure 1 to a GEOS-Chem simulation for the same period including interannual meteorological variability and driven by EPA trends in anthropogenic emissions of SO_2, NO_x, and VOCs (EPA 2015). We assume no trend in anthropogenic POA emissions because of large uncertainty, as discussed in the Introduction, and to focus on the impact of the biogenic OA component. Anthropogenic SOA in the model is solely from aromatic VOCs and the associated long-term trends are very small as reported below. Model results are obtained for successive summers (June–August 1991–2013) following one month of spinup each year for chemical initialization. GEOS-Chem is driven with meteorology from the NASA MERRA consistent reanalysis product covering 1991–2013

(https://gmao.gsfc.nasa.gov/reanalysis/MERRA/). The MERRA data are produced at 0.5° × 0.667° horizontal resolution and are re-gridded here to 2° × 2.5° for input to GEOS-Chem.

Annual US anthropogenic emissions of SO_2, NO_x, and VOCs are from EPA (2015) and are distributed spatially and temporally using the EPA National Emission Inventory for 2005 (EPA/NEI2005, https://epa.gov/pub/EmisInventory/nei_criteria_summaries/2005summaryfiles/). Anthropogenic emissions decreased over 1991–2013 by 3.3% a^{-1} for SO_2, 2.1% a^{-1} for NO_x, and 1.6% a^{-1} for VOCs. Anthropogenic emissions of ammonia are from NEI2005 and are constant over the period (Hidy *et al* 2014, Silvern *et al* 2016). POA emissions are from Bond *et al* (2007) for fossil fuel and biofuel combustion and from the annual Global Fire Emissions Database (GFED3) (van der Werf *et al* 2010) for open fires. Fuel POA emissions are assumed constant over the 1991–2013 period, as explained above, while open fire emissions vary from year to year on the basis of satellite data.

Isoprene, monoterpene, and sesquiterpene emissions are from the Model of Emissions of Gases and Aerosols from Nature (MEGAN2.1) (Guenther *et al* 2012); they vary locally as a function of leaf area index (LAI), temperature, and (for isoprene) solar insolation. LAI values are monthly means from the MODIS satellite instruments for 2000–2008 (Yang *et al* 2006), and the 2000–2008 mean is applied for the remainder of the 1991–2013 period. There is no significant regional trend in LAI over 2000–2008 and IAV is less than 4%. We assume no trend in vegetation type over 1991–2013. Interannual variability (IAV) in isoprene emission in the Southeast US is driven predominantly by temperature (Abbot *et al* 2003, Palmer *et al* 2006). We find that isoprene emission IAV over 1991–2013 of 12% can be explained by temperature ($R^2 = 0.81$ using GEOS-Chem isoprene emissions and MERRA temperature).

The GEOS-Chem simulation includes detailed aerosol-oxidant chemistry as described by Marais *et al* (2016) for their summer 2013 simulation over the Southeast US. SOA formation from anthropogenic and biomass burning VOCs, monoterpenes, and sesquiterpenes is by reversible partitioning of VOC oxidation products to pre-existing OA (Pye *et al* 2010). Isoprene SOA formation is by reactive uptake of isoprene oxidation products to aqueous aerosol and is coupled to a detailed gas-phase chemical mechanism for isoprene oxidation. The rate of reactive uptake depends on aqueous aerosol volume, and also for the IEPOX pathway on aerosol acidity (Eddingsaas *et al* 2010). GEOS-Chem isoprene SOA mass yields (3.3%) and composition, dominated by IEPOX (58% of isoprene SOA mass) and glyoxal (28%) as immediate precursors, are consistent with surface and aircraft observations for the summer 2013 (Marais *et al* 2016).

Isoprene SOA formation depends strongly on sulfate but is relatively insensitive to NO_x. Partitioning of isoprene oxidation between high-NO_x and low-NO_x pathways is only moderately dependent on anthropogenic NO_x emissions (Pye *et al* 2013, Zheng *et al* 2015). NO_x contributes to particle-phase organonitrate formation from oxidation of isoprene and monoterpenes by the nitrate radical (Boyd *et al* 2015, Xu *et al* 2015), but in the Southeast US organonitrates account for only 3%–8% of observed OA (Lee *et al* 2016), while IEPOX SOA accounts for 28%–32% of OA (Budisulistiorini *et al* 2013, Budisulistiorini *et al* 2015, Hu *et al* 2015).

We find in our model that isoprene SOA contributes on average 59% of total OA over the Southeast US in summer 1991–1995. Biogenic SOA from terpenes contributes an additional 13%, so that 72% of total OA is biogenic. The remaining 28% are contributed by anthropogenic and biomass burning (open fires and biofuel use) sources as POA (together 21%) and SOA (together 7%). By 2009–2013 biogenic SOA has declined to 62% of total OA (40% isoprene SOA; 22% terpene SOA) and the remainder is anthropogenic and biomass burning sources as POA (together 25%) and SOA (together 13%). This is consistent with the previous GEOS-Chem study by Kim *et al* (2015), which attributed OA over the Southeast US in summer 2013 as 42% from isoprene, 20% from terpenes, 28% anthropogenic, and 10% from open fires. Our results suggest that the biogenic contribution was greater in the past.

Aqueous aerosol volume used to compute the reactive uptake of isoprene SOA precursors (mostly IEPOX and glyoxal) is determined in GEOS-Chem from the mass concentrations of different aerosol components with relative humidity (RH) dependent hygroscopic growth factors from the Global Aerosol Data Set (GADS) (Koepke *et al* 1997). Sulfate growth factors are applied to sulfate-nitrate-ammonium (SNA) aerosol and OC growth factors are applied to OC. Most aerosol growth is associated with SNA aerosol because of its greater hygroscopicity. Aerosol acidity for IEPOX SOA formation is computed with the ISORROPIA thermodynamic equilibrium model (Fountoukis and Nenes 2007). Hygroscopic growth factors for sulfate from GADS and ISORROPIA agree within 10%.

1991–2013 model trends for the Southeast US in summer are shown in figure 1. The long-term declines over 1991–2013 are 2.4% a^{-1} for sulfate and 1.4% a^{-1} for OA, roughly consistent with observed trends from SEARCH and IMPROVE. The majority of the model trend in OA is driven by isoprene SOA, which declines by 2.2% a^{-1} as also shown in figure 1. The IEPOX SOA component similarly declines by 2.2% a^{-1}. In GEOS-Chem 1 μg decline in sulfate leads to a 0.35 μg decline in IEPOX SOA. This can be compared to the observed relationships between IEPOX SOA and sulfate of 0.42 $\mu g\ \mu g^{-1}$ at the Centreville, AL site (Xu *et al* 2015) and 0.23 $\mu g\ \mu g^{-1}$ from aircraft observations downwind of a power plant (Xu *et al* 2016). There is no significant

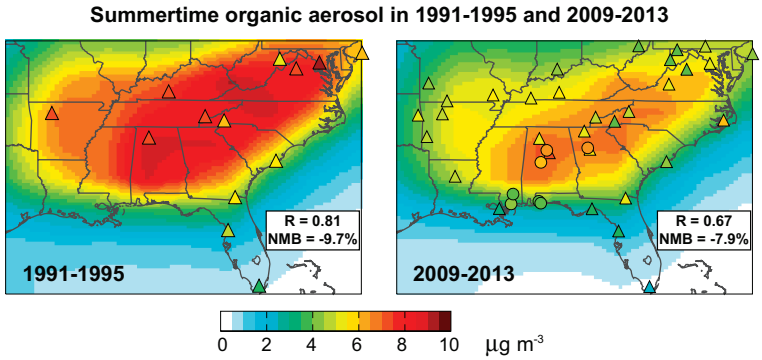

Figure 2. Spatial distribution of mean summertime (June–August) organic aerosol (OA) concentrations in 1991–1995 (left) and 2009–2013 (right). Surface observations from SEARCH (circles) and IMPROVE (triangles) are compared to GEOS-Chem (background). IMPROVE OA has been corrected for a 30% low bias (Ford and Heald 2013, Kim *et al* 2015). Pearson's correlation coefficients and model normalized mean biases (NMB) are shown.

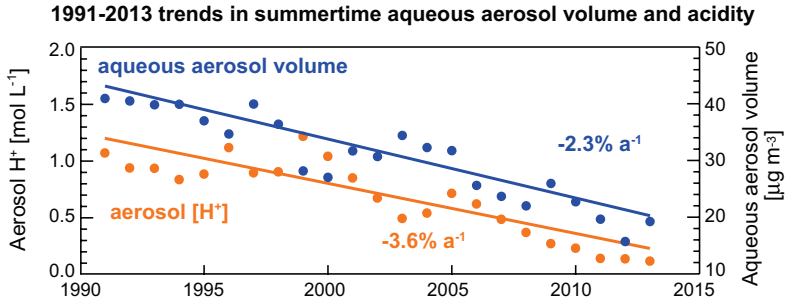

Figure 3. Simulated 1991–2013 trends in summertime (JJA) Southeast US aqueous aerosol volume mass concentrations and aerosol acidity. Values are from the GEOS-Chem model averaged over the domain in figure 1. Trends are obtained with the Theil-Sen estimator (Theil 1950) and are significant at the 95% confidence level.

model trend in OA from open fires, and decline in anthropogenic SOA due to decline in VOC precursor emissions is only 0.7% a^{-1}. SOA from terpenes increases by 1.7% a^{-1} due to increase in terpene SOA yields with decline in NO_x (Pye *et al* 2010), partly offsetting the isoprene SOA trend. As also shown in figure 1, the model trend in isoprene SOA is not seen if the aqueous-phase chemistry mechanism is replaced by the commonly used mechanism involving reversible partitioning of semivolatile oxidation products to pre-existing OA (Pye *et al* 2010).

We find in the model that isoprene SOA mass yields per unit isoprene oxidized decrease from 13% in 1991 to 3.5% in 2013. Decrease in NO_x emissions increases the isoprene SOA yield in the model, due to an increase in the formation of IEPOX under low-NO_x conditions, but the effect is small compared to that of SO_2. The branching ratio of the IEPOX-forming hydroperoxyl radical (HO_2) oxidation channel for isoprene peroxy radicals increases from 24% in 1991 to 32% in 2013. An isoprene SOA yield of 13% in 1991 is higher than the range (0.1%–10%) obtained for chamber studies reviewed by Marais *et al* (2016), but the chamber conditions are generally not representative of the atmosphere. Surratt *et al* (2010) reported a yield of 28% in an experiment under low-NO_x conditions using highly acidic inorganic seed aerosol.

Figure 2 compares the spatial distributions of observed and simulated OA over the Southeast US in summer for 1991–1995 and 2009–2013. The spatial pattern in the observations is consistent with a dominant biogenic source. The model normalized mean bias (NMB) is −9.7% in 1991–1995 and −7.9% in 2009–2013. Mean OA concentrations in the Southeast US decrease from 1991–1995 to 2009–2013 by 25% in the observations and 23% in the model. There is no significant change in spatial pattern, either in the observations or the model, offering supporting evidence that biogenic SOA is driving the trend.

4. Discussion

The decline in isoprene SOA is driven in the model by decreases in aqueous aerosol volume and acidity (figure 3) that are both driven in turn by decreasing SO_2 emissions. Aqueous aerosol volume mass concentration decreases by 54% over 1991–2013. Nguyen *et al* (2015) estimated a 79% decrease in aerosol water over 2001–2012 by applying ISORROPIA to the SEARCH observations. Decline in aerosol water mass concentrations in GEOS-Chem for the same time period is 40%. SEARCH sites show steeper decline in sulfate than the domain sampled by the

model and the IMPROVE network (figure 1). Aerosol acidity decreases by 83%. We conducted a separate GEOS-Chem simulation for summer 1991 using summer 2013 aerosol acidity and find that acidity alone is responsible for half of the long-term trend in isoprene SOA, with the rest due to decline in aerosol water. We further find in additional sensitivity simulations with aerosol $[H^+]$ fixed at 0.1, 0.2, 0.5, 0.8, and 1.1 mol l^{-1} that the relationship between isoprene SOA and aerosol acidity is logarithmic, due to limitation of the overall rate by mass accommodation of IEPOX at low pH. Within the above range, a decrease in aerosol pH of 0.1 increases isoprene SOA by ~0.2 μg m^{-3}.

Decline in aerosol acidity over 1991–2013 as shown in figure 3 would be expected from standard thermodynamics as sulfate decreases with constant ammonia. However, observations in the Southeast US in summer show that the ammonium–sulfate aerosol ratio is actually decreasing (Weber *et al* 2016). This decrease is inconsistent with simple SNA thermodynamics and might reflect an OA effect on the thermodynamics (Kim *et al* 2015, Silvern *et al* 2016).

We examined the implications of possible model error in the 1991–2013 trend of aerosol acidity. Assuming constant acidity in the model would decrease the isoprene SOA trend by half, as pointed out above, and would underestimate the observed trend in OA. This deficit could be compensated by a decline in anthropogenic POA or by a dependence of monoterpene and sesquiterpene SOA formation on aqueous aerosol volume, not included in our simulation. The laboratory study of Aljawhary *et al* (2016) suggests that aqueous-phase processing may be an important SOA formation pathway for monoterpenes. Glyoxal is an oxidation product of monoterpenes (Fu *et al* 2008, Chan Miller *et al* 2016) and would also contribute to dependence of monoterpene SOA on aqueous aerosol volume. Assuming that the terpene SOA yield increases linearly with aqueous aerosol volume (as for isoprene SOA) and the trend in isoprene SOA is due to aqueous aerosol volume only, we find that the deficit between the observed OA trend and the model could be compensated by an effective terpene SOA yield (mass SOA formed per unit mass of monoterpene/sesquiterpene oxidized) of 13% in 1991 dropping to 5% in 2013. This is within the range of terpene SOA yields measured in chamber studies (Ng *et al* 2007, Shilling *et al* 2008, Saathoff *et al* 2009, Fry *et al* 2014), although chamber conditions may differ from the actual atmosphere (Hallquist *et al* 2009).

We also examined the interannual variability (IAV) superimposed on the long-term trends (figure 1) to confirm the importance of biogenic SOA to the long-term trend. IAV should be driven mainly by weather, including effects on biogenic VOC emissions. Isoprene SOA IAV in the model accounts for 95% of the IAV in total OA and is correlated with the IAV in isoprene emission ($R = 0.68$). The model OA IAV, obtained as the relative departure from the regression line of long-term trends in figure 1, is correlated with the observed OA IAV at SEARCH ($R = 0.49$) and IMPROVE ($R = 0.55$), but is 60%–80% higher than the observations. The overestimate is due to very high model OA in 1998–2000 and 2005–2007 that is not seen in the observations. These years correspond to drought in the Southeast US (Seager *et al* 2009) that may suppress isoprene emission (Pegoraro *et al* 2004). This effect is not included in MEGAN as implemented in GEOS-Chem and thus model isoprene emission may be too high. OA IAV is correlated with mean surface air temperature both in the model ($R = 0.71$, using MERRA temperature) and in the observations ($R = 0.44$ at SEARCH sites using collocated temperature data; $R = 0.47$ at IMPROVE sites using temperature from nearby EPA monitoring sites).

In summary, observations of organic aerosol (OA) over the Southeast US in summer show a large 1991–2013 decrease. We find with the GEOS-Chem model that this trend can be largely explained by a decrease in the yield of secondary OA (SOA) from biogenic isoprene as SO_2 emissions have decreased. This decline in isoprene SOA yield in GEOS-Chem is based on an aqueous-phase mechanism for isoprene SOA formation that is dependent on aqueous aerosol volume and acidity, both of which decrease as SO_2 emissions decrease. Better understanding is needed of the factors controlling aerosol acidity and its trends in the Southeast US, and of the role of trends in anthropogenic emissions of OA and VOC precursors. Nevertheless, this study provides support that SO_2 emission controls to decrease sulfate aerosol have had a large co-benefit by concurrently decreasing OA.

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